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AMMONIA-NITROGEN REMOVAL BY BREAK-POINT CHLORINATION

Thomas A. Pressley, et al

District of Columbia Department of Environmental

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16. Abstract

In laboratory studies of breakpoint chlorination, sodium hypochlorite oxidized the ammonia in buffered distilled water (with 20 mg/l of NH_3-N), raw wastewater, lime clarified and filtered raw wastewater, secondary effluent and lime clarified and filtered secondary effluents to chiefly nitrogen gas. In the oxidation of this buffered water and the wastewaters, only small amounts of NO_3-N (0.3 mg/l at pH 5 to 2.0 mg/l at pH 8) and NCl_3-N (0.05 mg/l at pH 8 to 0.3 mg/l at pH 5) were produced. The oxidation of ammonia to N_2 gas was best accomplished in the pH range 6-8. A Cl:NH_3-N ratio of approximately 8:1 was sufficient for the buffered water and the highly treated wastewater. However, increasing Cl:NH_3-N ratios (8-10:1) were required as the degree of pretreatment of the wastewater decreased.

In the pilot breakpoint operation, chlorine gas with sodium or calcium hydroxide for pH control was efficiently mixed with filtered secondary effluent and with lime clarified and filtered raw wastewater. Greater than 95% of the NH_3-N was converted to N_2 gas. Operation at controlled pH greater than 6.0 and with low residuals of free Cl_2 (2 mg/l) produced essentially no nitrogen trichloride and modest amounts of NO_3-N (0.6 mg/l). (Kisenbauer - EPA)

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September 1973

AMMONIA-NITROGEN REMOVAL BY BREAKPOINT CHLORINATION

BY

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Contract No. 14-12-818
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ABSTRACT

In laboratory breakpoint chlorination, sodium hypochlorite oxidized the ammonia in buffered water (with 20 mg/l of NH_3-N) and in raw, secondary and lime clarified and filtered municipal wastewaters chiefly to N_2 gas with only small amounts of NO_3-N (0.2 mg/l at pH 5 to 2.0 mg/l at pH 8) and NCl_3-N (0.3 mg/l at pH 5 to 0.05 mg/l at pH 8). The oxidation of ammonia to nitrogen gas was best accomplished in a pH range 6-8 and for water or highly pretreated wastewater required a $Cl:NH_3$-N weight ratio of approximately 8:1. Higher $Cl:NH_3$-N ratios (8-10:1) were needed as the degree of pretreatment of the wastewaters decreased. The reaction of intermediate monochloramine and free chlorine was complete in less than one minute at pH 7.0.

In the pilot plant, gaseous chlorine with sodium or calcium hydroxide for pH control was efficiently mixed with filtered secondary and with lime clarified and filtered raw wastewater. The NH_3 was oxidized with greater than 95% conversion to N_2 gas. Operation at controlled pH greater than 6.0 and with low residuals of free Cl_2 (2 mg/l) produced essentially no nitrogen trichloride and modest amounts of NO_3-N (0.6 mg/l).

In the breakpoint chlorination of wastewaters, a split chlorine feed technique to utilize the alkalinity of the water and decrease the amount of base required in the process is described.

The instrumentation used in the control of the process and additional instrumentation designed and built by the EPA-DC Pilot Plant staff to fully automate the process is also described.

This report was submitted in partial fulfillment of Project 11010 EYM and Contract No. 14-12-818 by the Department of Environmental Services, Government of the District of Columbia under the sponsorship of the Environmental Protection Agency. Work was completed as of September 1971.

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Walter W. Schuk of the Environmental Protection Agency developed the control system described in the study and is acknowledged with sincere thanks.

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SECTION I

CONCLUSIONS

1. Ammonia in wastewater and water was oxidized by chlorine to chiefly nitrogen gas with a residual NH_3-N concentration of less than 0.1 mg/l. The chlorine was applied in the gaseous state to a stream of water and base before mixing with the wastewater, or as a solution of hypochlorite. The base was required to neutralize the acid produced in the reaction. The chlorine and base were premixed before addition to the wastewater and then completely and rapidly mixed with the wastewater in a breakpoint reactor.

2. In the laboratory on buffered aqueous systems, monchloramine concentrations increased with chlorine doses of up to about a 5:1 weight ratio of $Cl:NH_3$-N and then decreased to zero at the breakpoint dosage of at least 8:1 $Cl:NH_3$-N. Qualitatively, the formation of monochloramine and the reaction between intermediate monochloramine and free chlorine at pH 7.0 was completed in less than 1 minute.

3. In the aqueous systems, traces of dichloramine were produced in the 5-8 pH range. Nitrate and nitrogen trichloride were also produced. Potential products of N_2O, NO, and NO_2 were not detected.

4. In the buffered aqueous systems at the breakpoint, NO_3^- formation increased from 1.5% of the influent NH_3-N at pH 5 to about 10% at pH 8. Simultaneously, the NCl_3 formation decreased from 1.5% of the influent NH_3-N at pH 5 to 0.25% at pH 8.

5. In wastewater, the amount of NO_3^- formation was less (40-50%) than that in the aqueous system but varied with pH similar to the buffered aqueous system. Above pH 6.5 with proper mixing, the nitrogen trichloride formation in wastewaters and aqueous systems did not occur until after the chlorine dosage exceeded a 7.6:1 weight ratio of $Cl:NH_3$-N. In general in the pH range of 6-8, increasing the amount of excess free chlorine in the wastewater after breakpoint increased the amount of NCl_3 produced. Also, as in the aqueous system after the breakpoint, the formation of NCl_3 increased as the pH of the wastewater during the breakpoint process decreased.

6. In wastewater the formation of NCl_3 decreased with decreasing pretreatment. Indeed, in raw wastewater, $Cl:NH_3$-N dosages up to 12:1 did not produce NCl_3.

7. The $Cl:NH_3$-N weight ratio at breakpoint varied from approximately 8:1 to 10:1 for the wastewaters tested. Increased pretreatment reduced the amount of chlorine with lime clarified and filtered secondary effluents requiring an 8:1 $Cl:NH_3$-N dosage.

8. A temperature effect on the type and amount of reaction products did not occur in the 5°C to 40°C range.

9. With gaseous chlorine, the base required increased with final reaction pH. At pH 7 in secondary effluent, 1.3 pounds of NaOH were used per pound at Cl_2 (1.25 equivalent per equivalent of chlorine). Stoichiometrically, 1.5 pounds of NaOH per pound of Cl_2 were required to neutralize all the acid produced by the breakpoint. The difference between the base theoretically needed and that actually used was attributed to acid neutralization by the alkalinity of the secondary wastewater.

10. Since NCl_3 formation occurred when the $Cl:NH_3$-N ratio was greater than that needed for breakpoint, especially under acidic conditions, and NO_3 production increased at higher pH (8), care must be taken during the addition of base and chlorine to produce conditions that will minimize the production of either of these undesirable residuals. Breakpointing at a pH of approximately 7 with very careful control of excess free chlorine provided the best overall operation.

SECTION II

RECOMMENDATIONS

The stirred tank reactor employed in the study should be replaced by inline mixers which can efficiently and rapidly mix the chlorine with the wastewater. The chlorine dosing and the stability of the pH control loops should be evaluated with the inline mixer reactor.

Kinetic studies on the oxidation of monochloramine to nitrogen gas and on the by-product reactions are recommended to optimize reactor design.

The use of chlorine in the pH reduction step (10.0-7.0) liberates CO_2 which can be stripped out of the water. If the CO_2 is left in the water, part of the base added will react with it. Hence, the decrease in base usage with two stage chlorination with the intermediate CO_2 stripping should be evaluated.

Chlorine and CO_2 may be used to reduce the pH of the first stage lime clarified effluent from pH 11.5 to 7. For initial ammonia concentrations of up to 20 mg/l, the alkalinity ($\sim$300 mg/l as $CaCO_3$) of lime clarified water at pH 11.5 is sufficient to neutralize the acid produced by the breakpoint reaction. Thus the second stage clarification in the two stage lime clarification can be eliminated. This process alternate requires evaluation.

Instrumentation described in the report has been designed and built by the Pilot Plant Staff to completely automate the process. Evaluation of the instrumentation under continuous operating conditions is needed.

SECTION III

INTRODUCTION

Breakpoint chlorination, as practiced for many years in the water treatment industry provides a physical-chemical means for removing ammonia from wastewaters. In water, at NH_3-N concentrations usually below 1 mg/l, chlorine reacts with the ammonia to form various chloramines:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \qquad (1)$$

$$NH_4^+ + HOCl \longrightarrow NH_2Cl + H_2O + H^+ \qquad (2)$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O \qquad (3)$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O \qquad (4)$$

Chlorine is added to process waters until a point is reached where the total dissolved residual chlorine has reached a minimum (the breakpoint) and the NH_3-N has disappeared.

In water at NH_3-N concentrations of less than 1 mg/l, and before the breakpoint, the type of chloramine formed depends upon the pH. Spectrophotometric analyses (2, 4, 5, 12, 14) indicates that the chief constituent is monochloramine in the pH range of 7-8.5. As the pH decreases below 7, increasing amounts of dichloramine appear. In the pH range of 4.5-5.0, dichloramine is the chief product; below pH 4, nitrogen trichloride is the chief product.

Breakpoint chlorination studies (17) on buffered sunthetic ammonia samples at pH 7.0 reveal that the monochloramine concentration reaches a maximum at the 5:1 weight ratio of $Cl:NH_3$-N. As the weight ratio of $Cl:NH_3$-N exceeds 5:1, the monochloramine breaks down (6) to form dichloramine and ammonia according to equation 5.

$$2NH_2Cl \longrightarrow NHCl_2 + NH_3 \qquad (5)$$

The dichloramine reaches a maximum concentration at the $Cl:NH_3$-N weight ratio of about 7.5:1.

The literature (7) indicates that in water with less than 1 mg/l of NH_3-N, the reaction proceeds in competition with monochloramine formation (equation 2) until the chlorine dosage reaches the breakpoint at approximately a 10:1 weight ratio of $Cl:NH_3$-N. Other studies, (3, 14) however, indicate that monochloramine is oxidized by excess chlorine under slightly alkaline conditions to nitrogen gas as shown in equation 6.

$$2NH_2Cl + HOCl \longrightarrow N_2 + 3HCl + H_2O \qquad (6)$$

Stoichiometrically, the ammonia oxidation through monochloramine to N_2 corresponds to a 7.6:1 weight ratio of $Cl:NH_3$-N. The literature (2, 4, 7, 14) also suggests the occurence of other end-products, including nitrate as shown in equation 7 and nitrogen trichloride. In fact, the nitrogen trichoride produced (equation 4) in water treatment plants (10) during breakpoint chlorination has been a serious problem.

$$4HOCl + NH_3 \longrightarrow HNO_3 + 4HCl + H_2O \qquad (7)$$

In wastewaters, the NH_3-N concentration may be more than an order of magnitude higher than those normally encountered in natural waters. For use of breakpoint chlorination for nitrogen removal at the NH_3-N concentrations encountered in wastewaters, the end products of the reaction need to be known. This study identified the major products of the breakpoint reaction in synthetic buffered solutions and in wastewaters and determined the formation and behavior of the the undesirable residuals of NCl_3 and NO_3^- as a function of pH, chlorine dosage, and temperature in both laboratory the pilot plant studies.

SECTION IV

EXPERIMENTAL

The laboratory chlorination studies were performed in synthetic buffered aqueous systems, to eliminate effects from other substances reacting with chlorine, usually with initial NH_3-N concentrations of 20 mg/l, and in raw, secondary and lime clarified municipal wastewaters with NH_3-H concentrations ranging from 8-15 mg/l.

In end product identification studies on buffered aqueous systems, the gaseous products were qualitatively analyzed for N_2, O_2, and N_2O. The procedure involved purging the aqueous sample, containing 20 mg/l NH_3-N and buffered at pH 7.5, with helium to remove atmospheric nitrogen in a closed system attached to a gas chromatograph. The sample was then treated with nitrogen-free standard sodium hypochlorite at a dosage equal to a 10:1 weight ratio of Cl:NH_3-N. The gaseous products of the reaction were then flushed through the gas chromatograph with helium.

A test was also performed to identify the presence of any nitric oxide (NO) or nitrogen dioxide (NO_2). An enclosed breakpoint chlorinated sample was purged with air into a cold solution of 0.2N H_2SO_4 to remove any NO or NO_2 formed during the chlorination. In the procedure, (13) the NO was oxidized to NO_2 by the oxygen in the air and absorbed in the 0.2N H_2SO_4 as nitrous and nitric acids. The 0.2N H_2SO_4 solution was then analyzed for (NO_3^- + NO_2^-)-N.

Spectrophotometric scanning of both chlorinated aqueous samples and their CCl_4 extracts was also performed to determine other end-products. The samples, after two hours of contact with the chlorine, were placed in a recording spectrophotometer and scanned over the spectral range of 200-500 mg/l.

In the quantitative studies, aqueous ammonia or wastewater samples were manually mixed in separatory funnels with increasing dosage of standard sodium hypochlorite over the pH range of 5-8. A two hour contact time (17) was provided for all systems. The samples, after chlorination, were analyzed for (NO_3^- + NO_2^-)-N, NCl_3-N, NH_3-N, NH_2Cl and $NHCl_2$-N, TKN, total residual chlorine, free available chlorine and pH.

Quantitative temperature studies were also conducted at 5, 15, 25, and 40°C on aqueous ammonia samples containing 20 mg/l NH_3-N and buffered at pH 6.0 to determine temperature effects on the end-products. Multiple samples in separatory funnels were collected at the designated temperature in a constant temperature bath and treated with increasing dosages of pre-cooled sodium hypochlorite. The samples were then manually mixed and allowed to stand at the selected temperature for two hours before analysis.

The pilot chlorination reactor, designed after completion of the laboratory studies, was a 1200 gal. vessel, 4 ft. in diameter and 12 ft. tall. This reactor is shown in Figure 1. The reaction chamber in the bottom 3 ft. of the vessel (310 gal.) was divided into three equal sections separated by epoxy coated plywood inserts. In each section, a propeller mixer mounted on a common shaft, driven by a 3 h.p. motor, was rotated at 224 r.p.m. The influent entered at the top of the reactor. A pump on the effluent stream recycled 11 gal./min into the first mixing stage. Chlorine was added into the recirculation loop through a Wallace and Tiernan V-Notch chlorinator and injector nozzle. The dosage rate could be manually set to provide up to 12:1 Cl:N ratio by weight. The reaction pH was maintained automatically by pumping a 1 to 2% NaOH solution into the line ahead of the chlorine injector. The base and Cl_2 were premixed before addition to the wastewater. The NaOH feed was controlled by an inline pH probe on the discharge effluent using a variable stroke positive displacement pump.

Initial runs were made on filtered secondary effluent at constant flow rates that ranged between 25 and 35 gpm. The average feed concentration of BOD, COD, TOC and suspended solids was 16 mg/l, 41 mg/l, 18 mg/l and 25 mg/l respectively. The pH ranged from 7.0 to 7.3 with an alkalinity of 120-150 mg/l as $CaCO_3$. Later the system was run continously, usually at 25 gpm on lime clarified and filtered wastewater having a pH 9.3-9.9, phenolphthalein alkalinity in the 50-70 range, and methyl orange alkalinity in the range of 80-140 mg/l as $CaCO_3$.

The study required field measurements for NH_3-N which were made using a specially programmed Technicon Automatic Analyser. Free and combined chlorine were measured by the Modified Palin Method. During the later part of the study the free residual chlorine was monitored continuously using another Technicon Automatic Analyser. Nitrogen trichloride and nitrate formation were measured periodically in the laboratory.

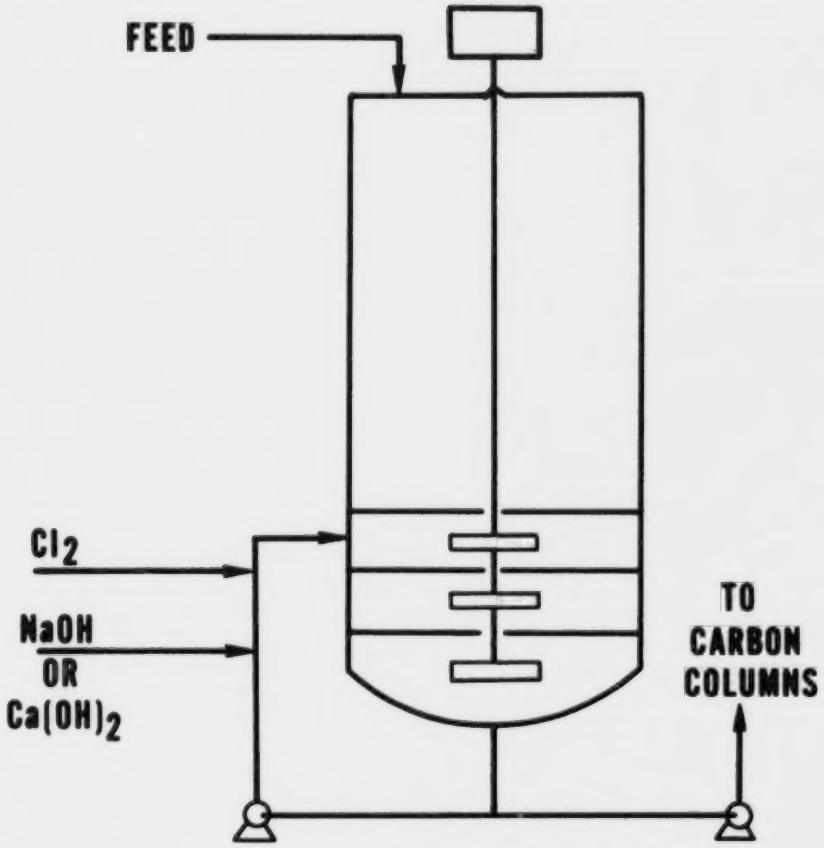


FIGURE 1 Breakpoint Chlorination Reactor

SECTION V

ANALYTICAL PROCEDURES

A modified automated hydrazine reduction method (9) with an alkaline digestion to eliminate chloramine interferences was used for the $(NO_3^- + NO_2^-)$-N analysis. In this procedure, the sample was made alkaline with NaOH, digested to dryness, redissolved and neutralized with HCl and diluted to volume for analysis. This modified procedure was reliable to $\pm$ .05 mg/l.

Nitrogen trichloride was analyzed in the synthetic ammonia samples and in wastewater samples by both the spectrophotometric procedure of Czeh et al. (5) and the Modified Palin Method (16). The results of spectrophotometric analysis of NCl_3 on wastewater samples were reproducible to $\pm$ .05 mg/l NCl_3-N. While analyses from the Palin Method were similar to those from the spectrophotometric procedure, they were poorly reproducible; therefore, the analyses from the spectrophotometric procedure were employed in the evaluation of the breakpoint studies on wastewaters. The spectrophotometric procedure for the analysis of NCl_3, however, represented all compounds extracted from the wastewater that absorb at 265 and 345 mμ in CCl_4.

Free available chlorine, mono and di-chloramine were analyzed according to the Modified Palin Method (16) with N, N-diethyl-p-phenylenediamine oxalate as the indicator, and by amperometric titration (15). All other analyses employed the procedures of "Standard Methods for the Examination of Water and Wastewaters" (15).

A Varian Aerograph Gas Chromatograph (Model 1532-2B) equipped with an ionization detector (with a tritium source) and a molecular sieve type column, designed to detect N_2, O_2, and N_2O, was used to qualitatively analyze the gaseous product. A Forma (Model 2095) circulating-constant temperature bath was used to control the temperature of the studies to $\pm$ 0.1°C U.V. absorbancies were determined on a Beckman DU Spectrophotometer or on a Beckman DBG recording Spectrophotometer, both with 10 mm quartz cells.

The NCl_3 standard was prepared by the method of Noyes (1) and assayed. Aliquots of the stock were diluted in carbon tetrachloride to make standard solutions ranging from 0-100 mg/l NCl_3. The NCl_3 standards scanned in the spectrophotometer produced peaks only at 265 and 345 mμ with linear absorbancies for increasing NCl_3 concentrations. The molar absorptivities calculated from the standards were 228 for the peak at 345 mμ and 445 for the peak at 265 mμ. The molar absorptivities reported by Czeh, Fuchs, and Antczak (5) were 232 for the peak at 345 mμ and 450 for the peak at 265 mμ.

Spectrograde CCl_4 was used throughout the study for extraction and dilution of standard and unknown samples. All other reagents used in the study were of reagent quality.

SECTION VI

REACTION PRODUCTS, pH AND TEMPERATURE

Reaction Products

In laboratory studies on buffered solutions at pH 7.5 with 20 mg/l of NH_3-N, spectrophotometric scans (200-500 mμ) of the buffered solution treated with increasing dosages of chlorine up to $Cl:NH_3$-N weight ratio of 7.5:1 revealed adsorption peaks at 243 mμ for monochloramine (11) and at 205 mμ for nitrate (15). Above the 7.6:1 ratio the peak at 243 mμ disappeared and a peak at 287 mμ appeared and increased with increasing chlorine doses. The control sample containing only the buffered solution with free chlorine and without NH_3-N, produced a peak only at 287 mμ. Thus, the peak at 287 mμ above the 7.6:1 ratio of $Cl:NH_3$-N was produced by free chlorine.

The absorbance produced by monochloramine at 243 mμ increased linearly with increasing chlorine dosages to a maximum at the 5:1 weight ratio of $Cl:NH_3$-N and then decreased to near zero at approximately the 7.6:1 ratio. The strong peak produced by NO_3^- at 205 mμ increased with increasing chlorine dosage through the 12:1 weight ratio of $Cl:NH_3$-N and confirmed the formation of NO_3^- during chlorination. In summary, spectral scanning of the aqueous ammonia solutions with different dosages of sodium hypochlorite indicated only the formation and decomposition of monochloramine, the gradual formation of NO_3^--N and the presence of free available chlorine after the breakpoint.

The CCl_4 extracts, scanned in the spectrophotometer in the range of 200-500 mμ against a reference control blank, produced strong NCl_3 peaks (5) at 265 and 345 mμ only after the chlorine dosage exceeded the 7.6:1 weight ratio of $Cl:NH_3$-N. At pH 6 and below measurable but small amounts of NCl_3 were detected below the 7.6:1 weight ratio of $Cl:NH_3$-N.

Gas chromatographic analysis for N_2, O_2 and N_2O at the breakpoint detected only N_2. Since O_2 was not detected, the formation of N_2O with subsequent decomposition to N_2 and O_2 did not occur. The tests for nitric oxide (NO) and nitrogen dioxide (NO_2) revealed that neither of these compounds were present. Qualitatively, the reaction of intermediate monochloramine and free chlorine was completed in less than one minute. Rate of formation of N_2 was not determined.

pH and Temperature

The addition of chlorine to buffered aqueous samples containing 20 mg/l NH_3-N at pH 7.0 produced a typical breakpoint curve with the complete

removal of the ammonia and a minimum total residual chlorine concentration of about 0.6 mg/l at approximately 8:1 weight ratio of $Cl:NH_3$-N (Figures 2 and 3). The chlorination studies of buffered solutions at pH 7.0 containing 1 mg/l NH_3-N also reached the breakpoint at approximately an 8:1 weight ratio of $Cl:NH_3$-N. In all tests on buffered aqueous systems in the pH range of 6-7, the breakpoint occurred at chlorine doses approximately equal to an 8:1 (stoichiometric ratio 7.6:1 equations 2 and 6) weight ratio of $Cl:NH_3$-N. Outside of the 6-7 pH range, the chlorine dose required for the breakpoint increased as shown in Figure 2.

In pH studies on synthetic samples containing 20 mg/l NH_3-N, the formation of NO_3^--N at the breakpoint (Figure 4) increased with increasing pH from about 0.3 mg/l (1.5% of the NH_3-N) at pH 5.0, to about 2.0 mg/l (10% of the NH_3-N) at pH 8.0. With increasing chlorine dosages above the breakpoint, the NO_3^--N formation increased sharply at pH 6.0 and above, but increased only slightly in the pH range of 5-6. Thus, low pH (5-6) produced minimum amounts (0.3 mg/l) of NO_3^--N.

In contrast, the amount of NCl_3-N formed at the breakpoint decreased from approximately 0.3 mg/l (1.5%) at pH 5.0 to 0.05 mg/l (0.25%) at pH 7 or 8 as seen in Figure 5. In the pH range of 7-8, a NCl_3-N concentration of less than 0.1 mg/l occurred at the breakpoint. As chlorine dosages exceeded the breakpoint, the formation of NCl_3 increased sharply at and below pH 7.0. At pH 8.0, however, the NCl_3 concentration increased but never exceeded approximately 0.3 mg/l for chlorine dosages up to a 12:1 weight ratio of $Cl:NH_3$-N. With NCl_3, which has a greater nuisance potential than nitrate, chlorination at the 9:1 weight ratio of $Cl:NH_3$-N (slightly above the breakpoint) minimized NCl_3 residuals at pH 8 but maximized nitrate formation as shown in Figure 6.

The 0.05 mg/l of NCl_3 at the breakpoint (produced by the oxidation of dichloramine) (6) also indicated only small amounts of dichloramine formed above pH 7. The modified Palin Analysis for dichloramine revealed less than 0.1 mg/l $NHCl_2$-N above pH 7 after 2 hours of contact time for all chlorine dosages.

Breakpoint chlorination studies on buffered aqueous systems at pH 6.0 were conducted in the temperature range of 5-40°C. These tests did not reveal significant changes in the reaction products after the 2 hour contact time. Complete removal of the NH_3-N was achieved at all temperatures as seen in Table 1.

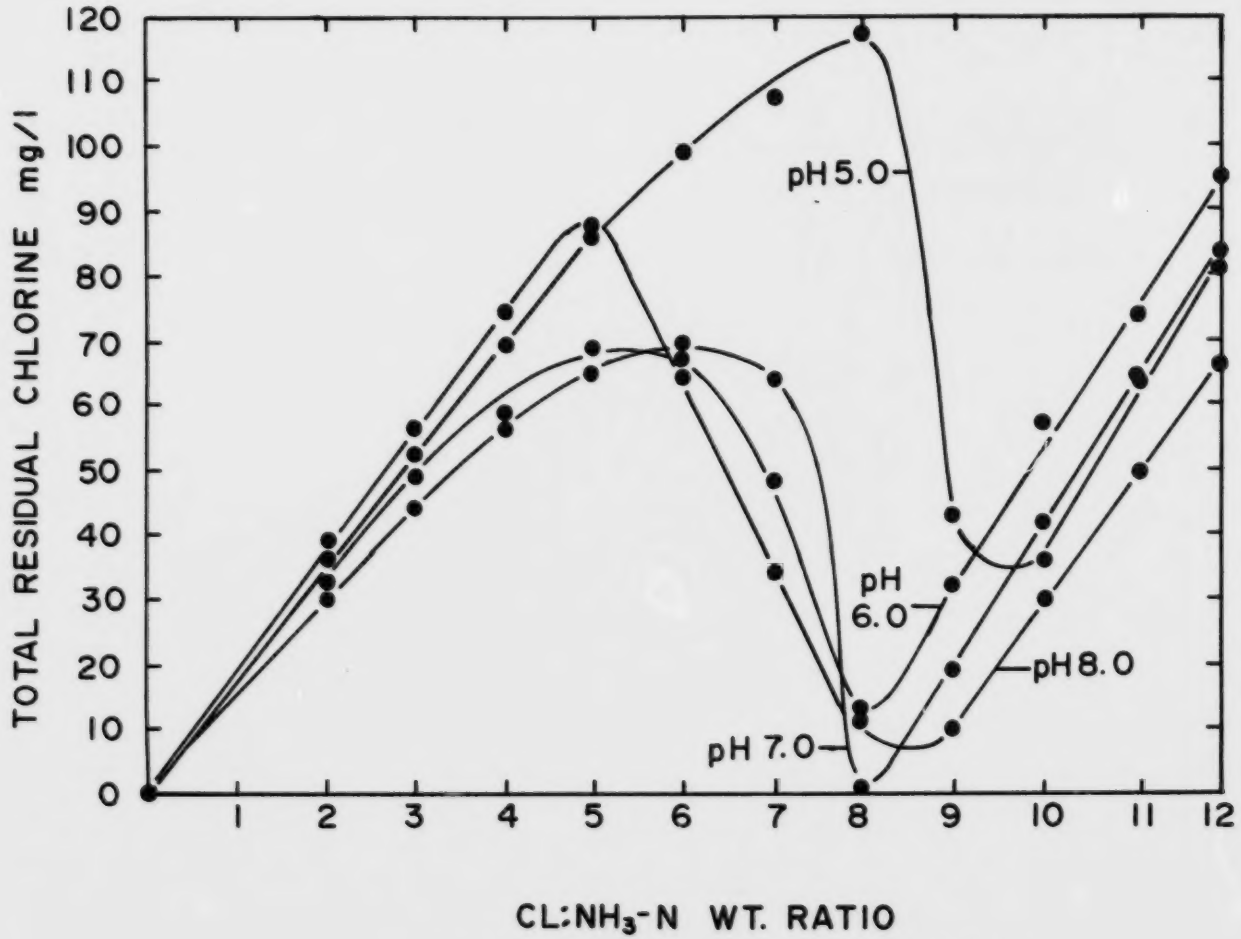


FIGURE 2 Breakpoint in Buffered Aqueous Systems

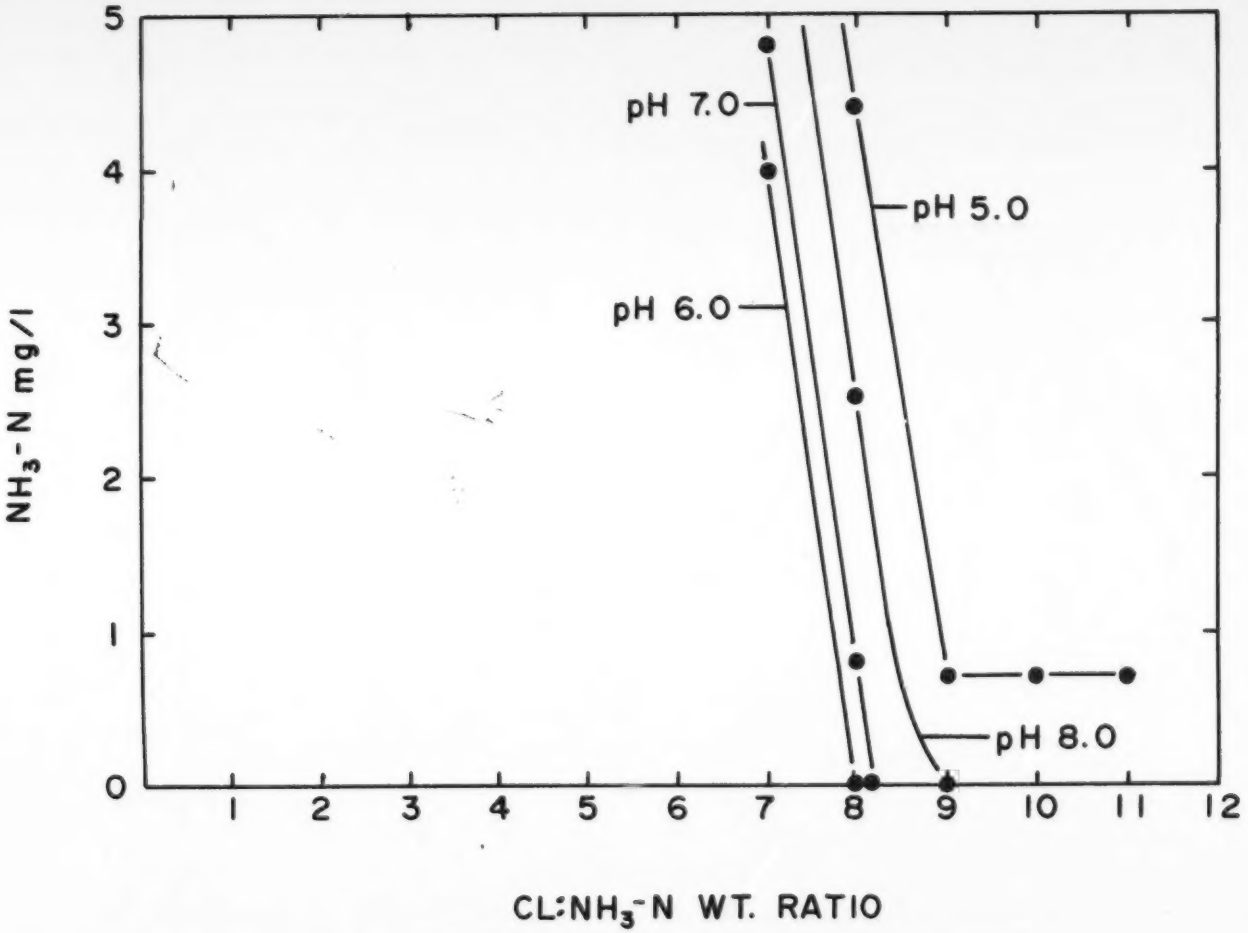


FIGURE 3 Ammonia Removal at Breakpoint

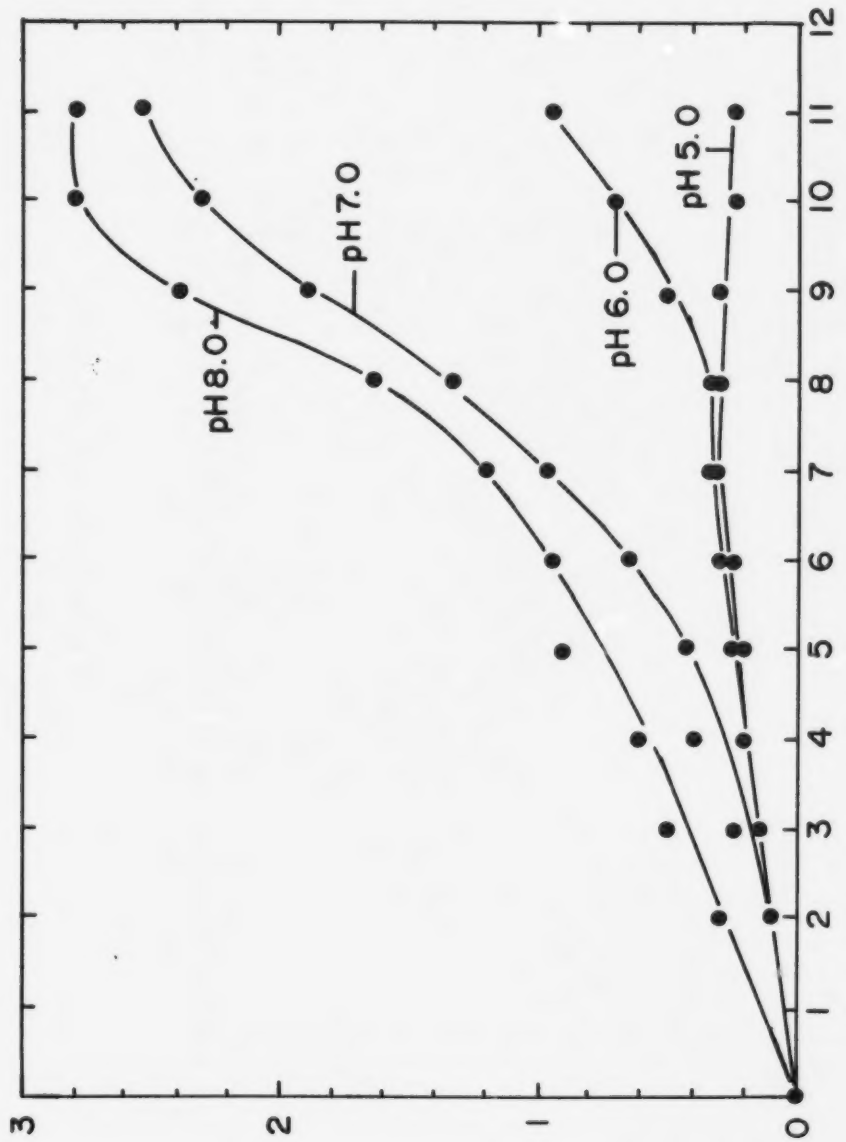


FIGURE 4 pH and Nitrite + Nitrate Formation

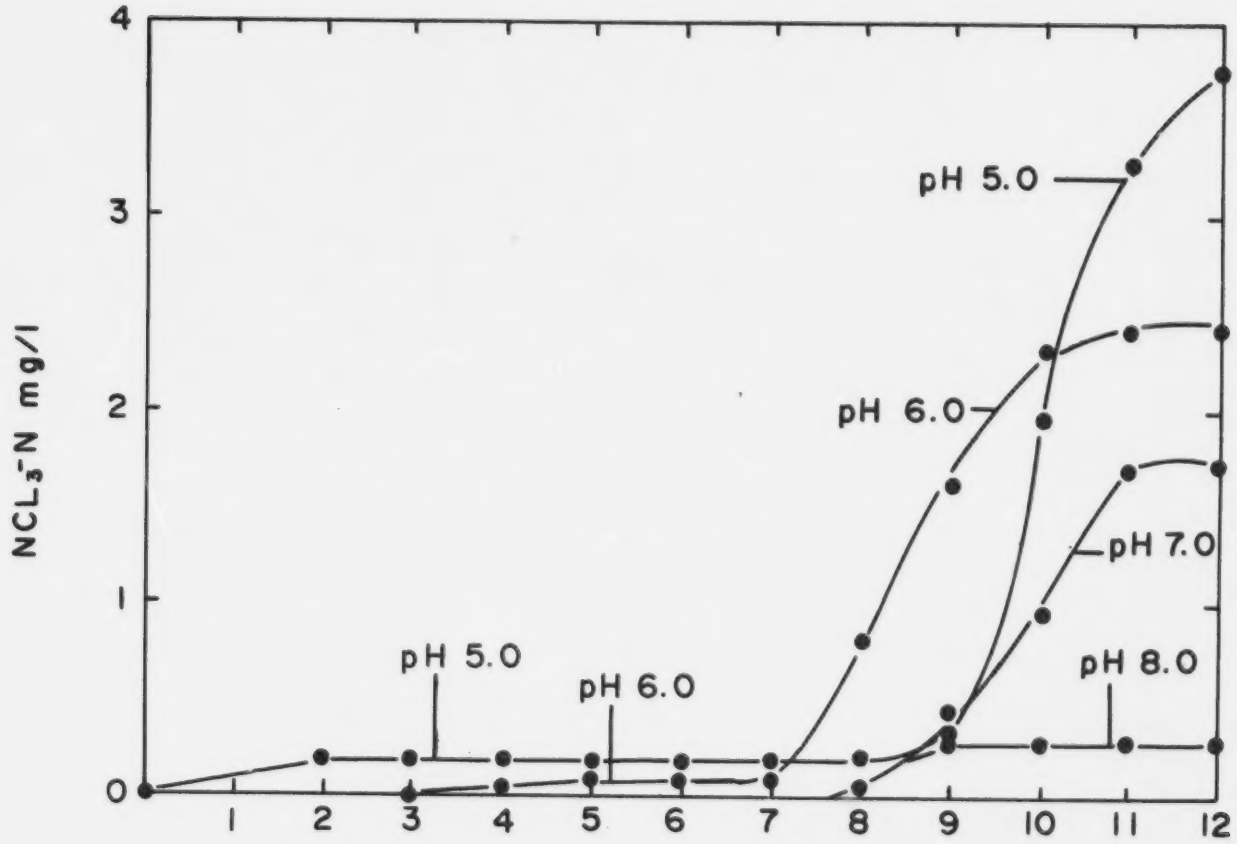


FIGURE 5 pH and Nitrogen Trichloride Formation

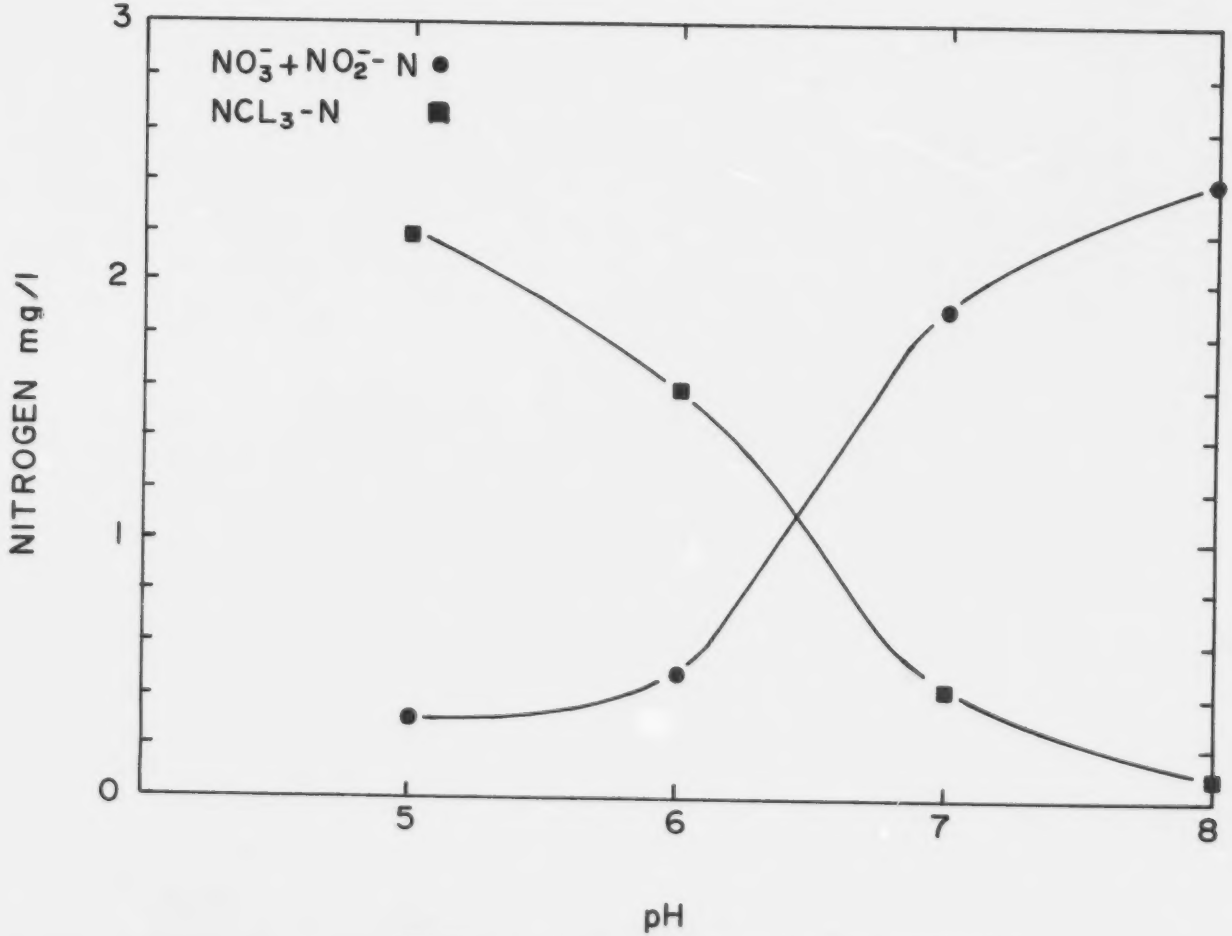


FIGURE 6 pH and Byproducts After Breakpoint

TABLE 1

BREAKPOINT CHLORINATION
TEMPERATURE STUDIES

pH = 6 *Contact Time = 2 hours*

Temp.	$Cl:NH_3$-N wt. ratio	NH_3-N mg/l	$(NO_3^- + NO_2^-)$-N mg/l	NCl_3-N mg/l
5°C	0	20.0	0.00	0.00
	5:1	9.20	0.10	0.00
	6:1	6.10	0.18	0.00
	7:1	1.19	0.27	0.00
	8:1	0.00	0.43	1.10
	9:1	0.00	0.50	1.89
	10:1	0.00	0.60	3.91
	11:1	0.00	0.70	5.67
15°C	0	20.0	0.00	0.00
	5:1	9.69	0.05	0.00
	6:1	6.00	0.05	0.00
	7:1	1.22	0.16	0.00
	8:1	0.00	0.30	1.10
	9:1	0.00	0.43	1.90
	10:1	0.00	0.52	3.90
	11:1	0.00	0.60	5.67
40°C	0	20.0	0.00	0.00
	5:1	9.20	0.00	0.00
	6:1	6.70	0.10	0.00
	7:1	3.90	0.15	0.00
	8:1	0.00	0.42	1.10
	9:1	0.-0	0.47	1.92
	10:1	0.00	0.55	4.00
	11:1	0.00	0.66	5.70

SECTION VII

LABORATORY CHLORINATION OF WASTEWATERS

In laboratory breakpointing of unclarified and lime clarified raw and secondary wastewaters (NH_3-N concentrations of 8-15 mg/l) with sodium hypochlorite, the $CaCO_3$ alkalinities of 80-120 mg/l in the water maintained the pH of all the samples between 6.5 and 7.5. The chlorine demand required for the breakpoint decreased and approached the stoichiometric amount (equation 2 and 6) for oxidation of NH_3 to N_2 as the degree of wastewater pretreatment increased. As an example, a chlorine dosage equivalent to a 10:1 weight ratio of $Cl:NH_3$ was required to breakpoint raw wastewater (Figure 7), while a 9:1 weight ratio was required in the secondary effluent (Figure 8), and about an 8:1 weight ratio of $Cl:NH_3$-N for lime clarified and filtered secondary effluent (Figure 9).

Total kjeldahl nitrogen analyses revealed nearly complete removal of the NH_3-N, but only a slight reduction of the organic nitrogen within the two hour contact time (Figures 7, 8, 9, 10). The nuisance residuals of nitrate and nitrogen trichloride-nitrogen at the breakpoint were always less than 1 mg/l (Figures 11, 12, 13, 14). In the 6.5-7.5 pH range, NCl_3 formation did not occur until the $Cl:NH_3$-N weight ratio exceeded a 7.6:1 dosage. The amount of NCl_3 also decreased with decreasing wastewater pretreatment, and did not occur in the raw wastewater. The breakpoint process removed only ammonia nitrogen. There was essentially no change in the organic nitrogen concentration.

If chlorine is employed rather than sodium hypochlorite, the breakpoint chlorination of ammonia concentrations normally encountered in wastewaters may produce more acid than can be neutralized by the buffer capacity of the wastewater, Stoichiometrically (equation 1, 2, and 6) 14.28 mg/l of $CaCO_3$ alkalinity (1.5 lb of NaOH/lb of Cl_2 used) are required to neutralize the acid produced by the oxidation of one mg/l NH_3-N to N_2. Therefore, a lime clarified secondary wastewater containing 20 mg/l NH_3-N requires approximately 160 mg/l of chlorine for breakpointing and an alkalinity of about 286 mg/l. Since the amount of NCl_3 formed before the breakpoint increases with decreasing pH, any excess acid produced must be neutralized with base and proper mixing to avoid both excess local chlorine concentrations and low pH.

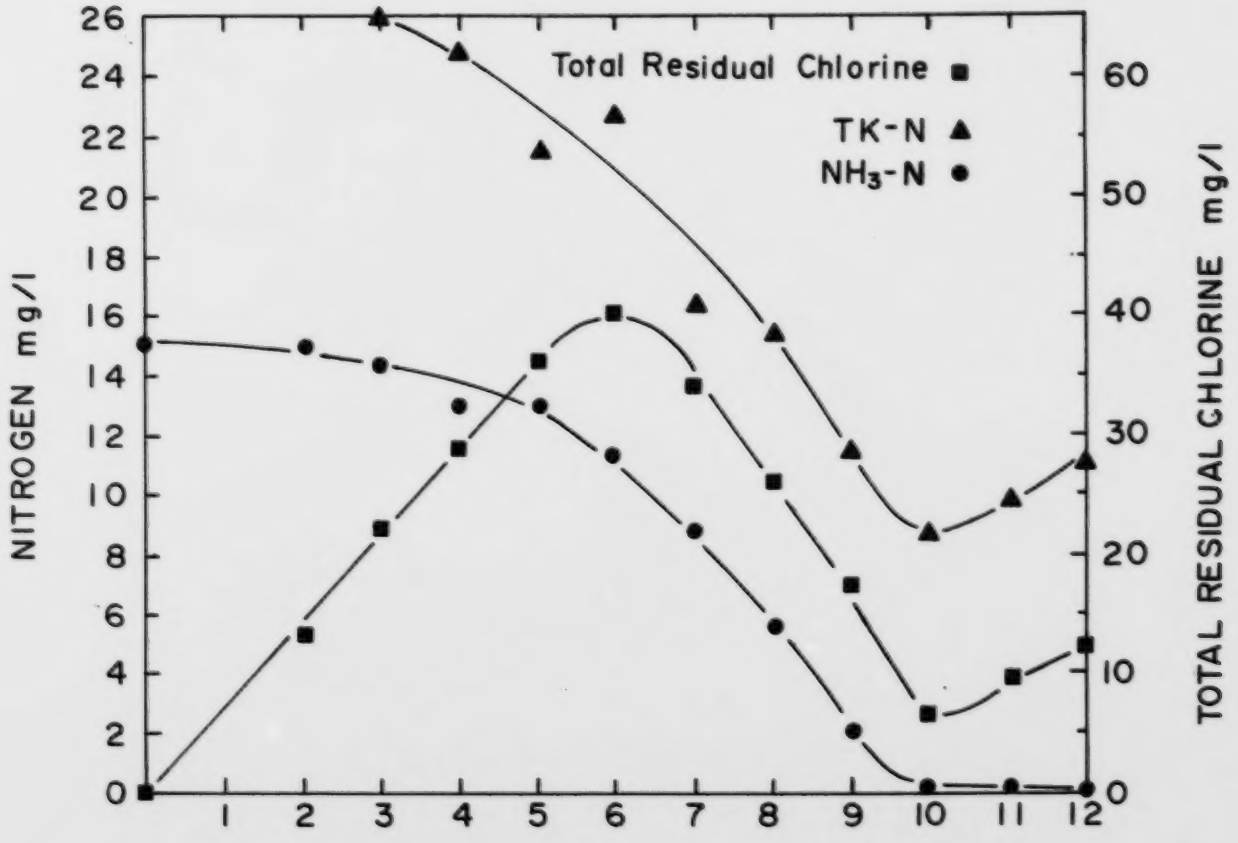


FIGURE 7 Breakpoint in Raw Wastewater

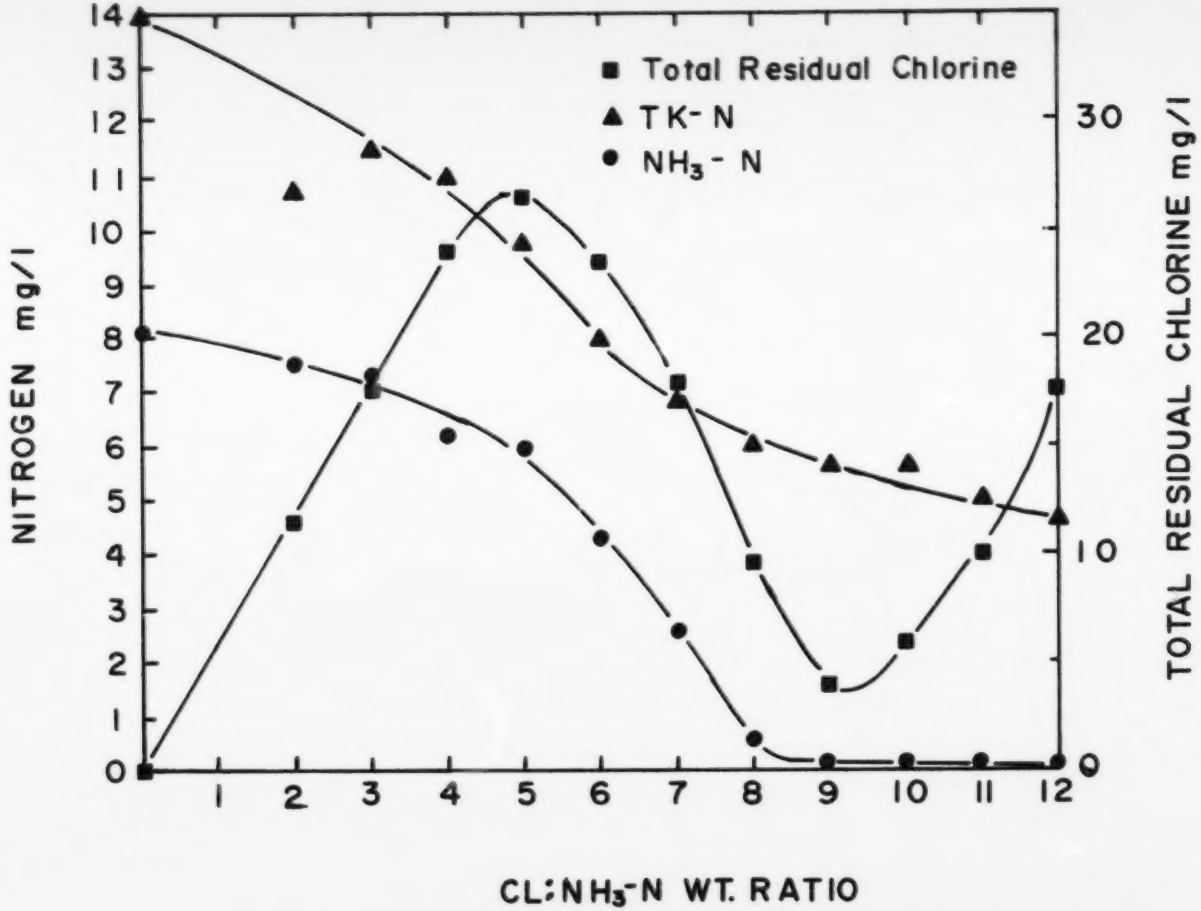


FIGURE 8 Breakpoint in Secondary Effluent

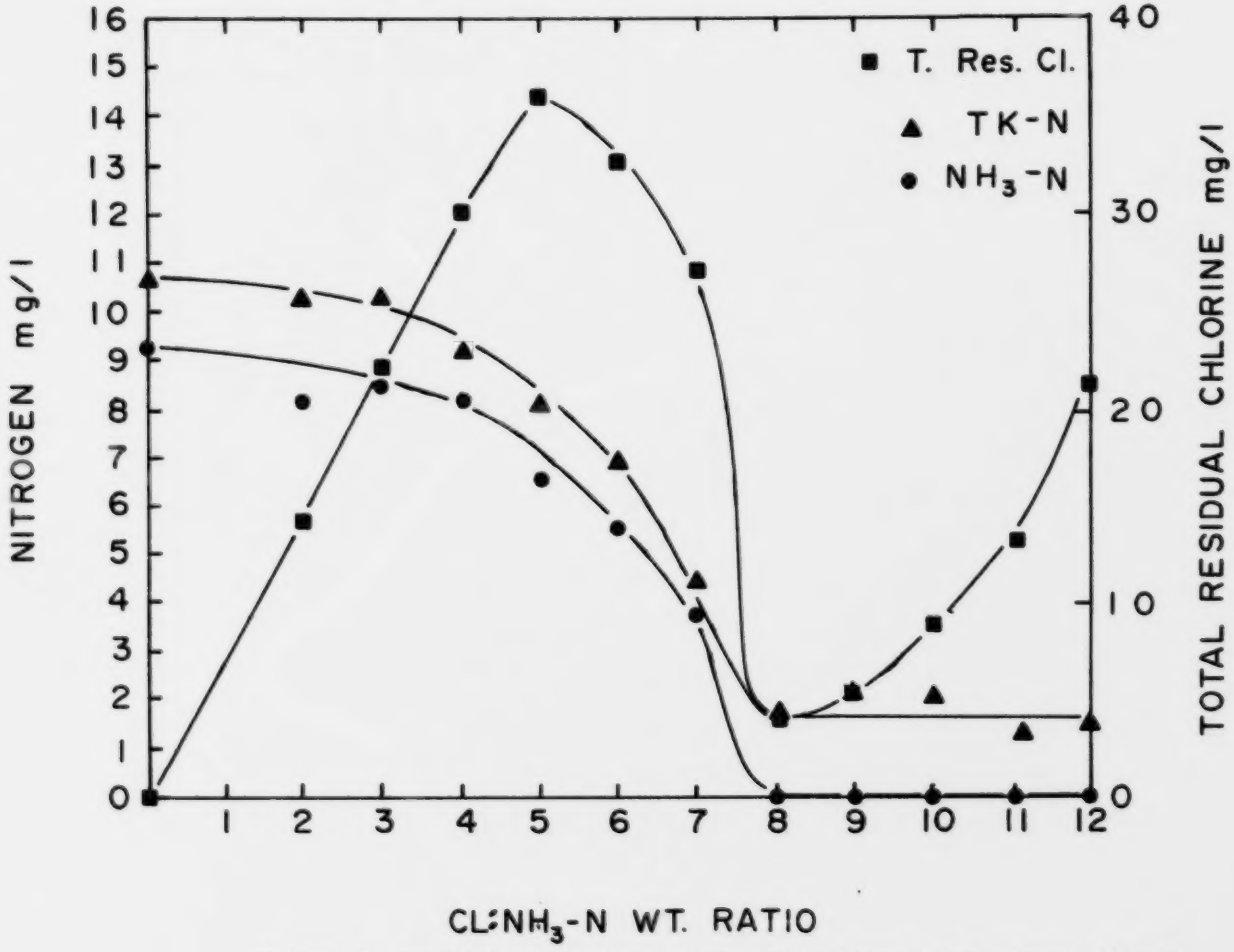


FIGURE 9 Breakpoint in Lime Clarified Filtered Secondary Effluent

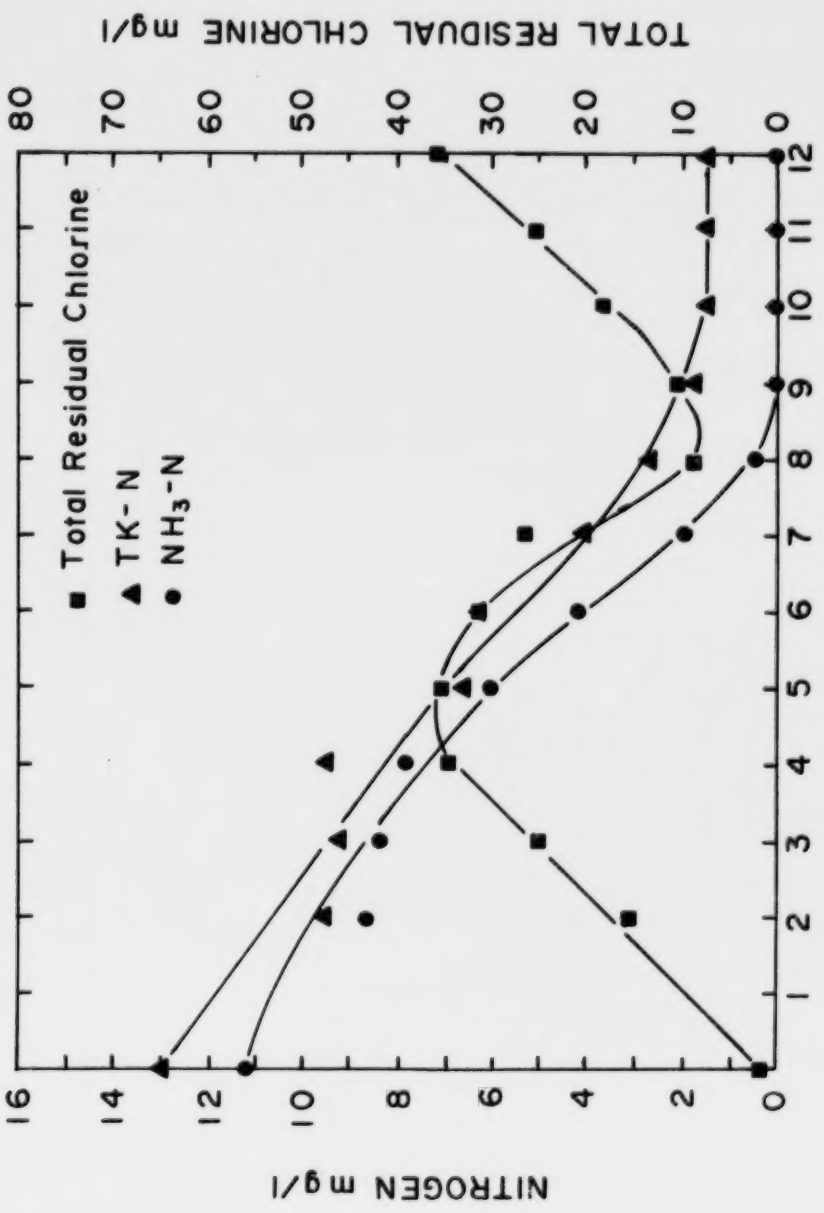


FIGURE 10 Breakpoint in Lime Clarified Filtered Raw Wastewater

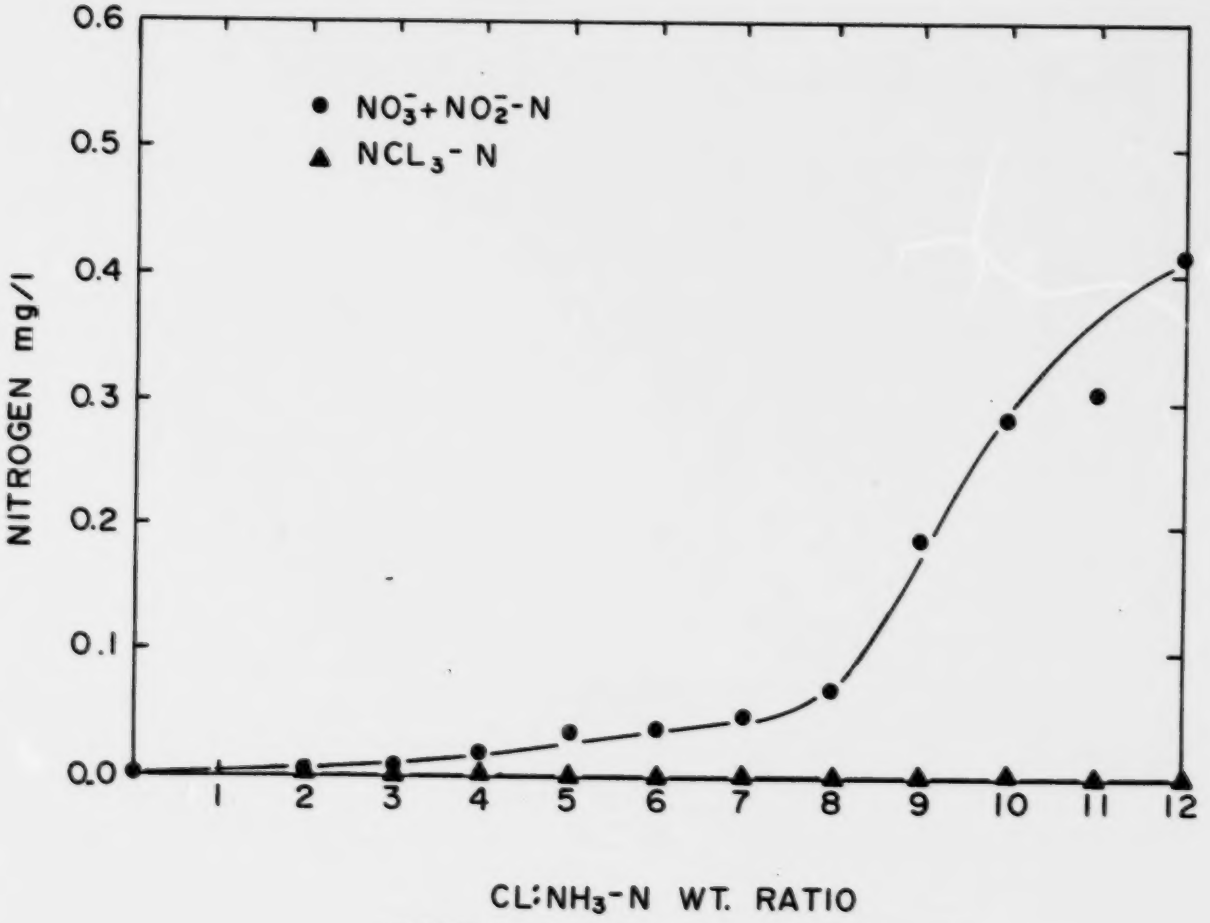


FIGURE 11 Byproducts in Raw Wastewater

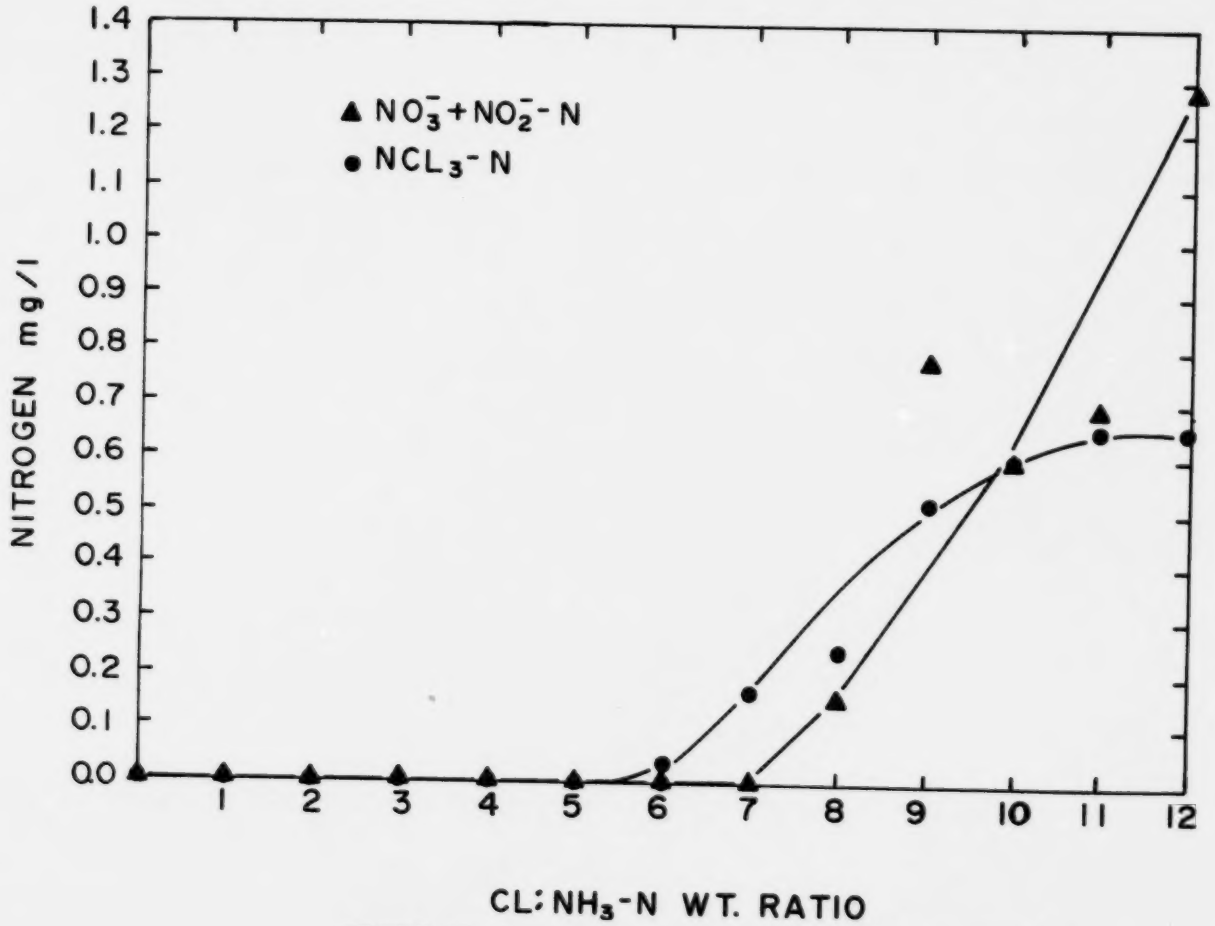


FIGURE 12 Byproducts in Lime Clarified Raw Wastewater

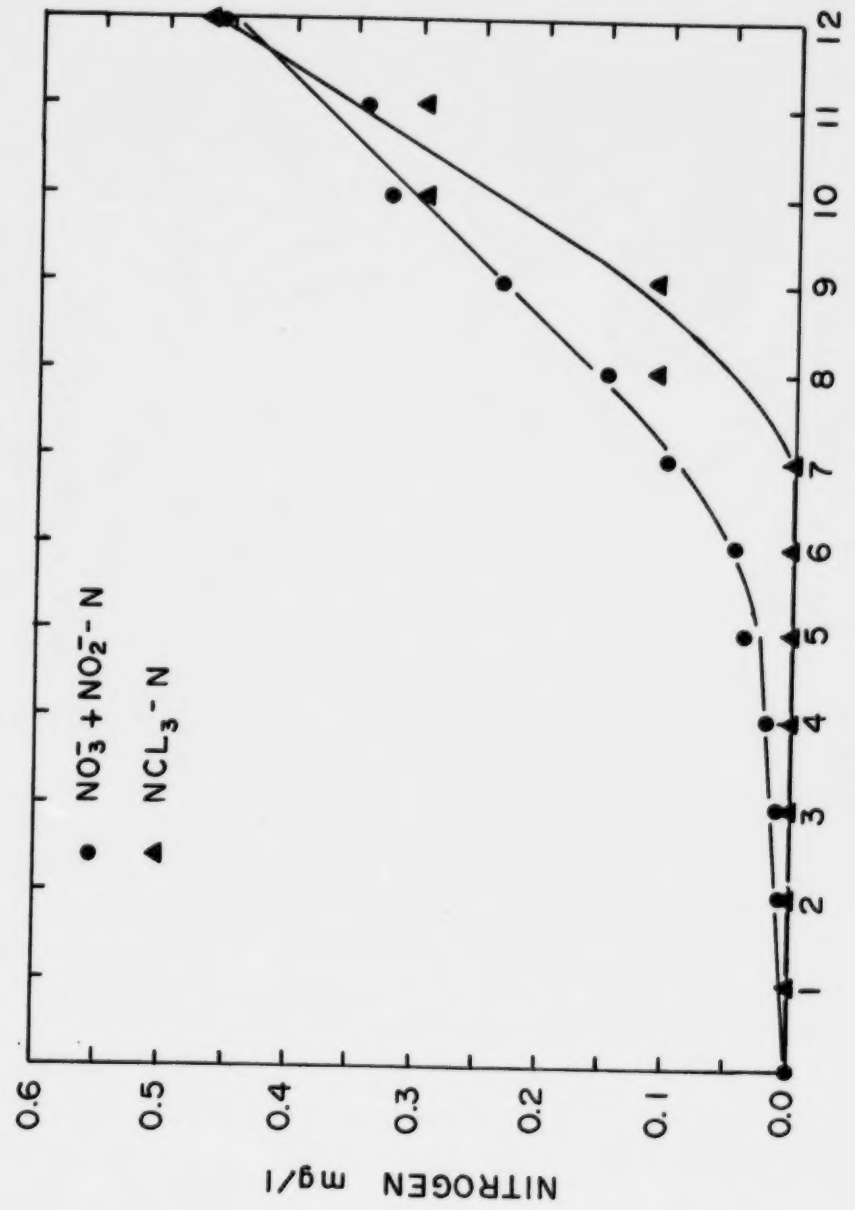


FIGURE 13 Byproducts in Secondary Effluent

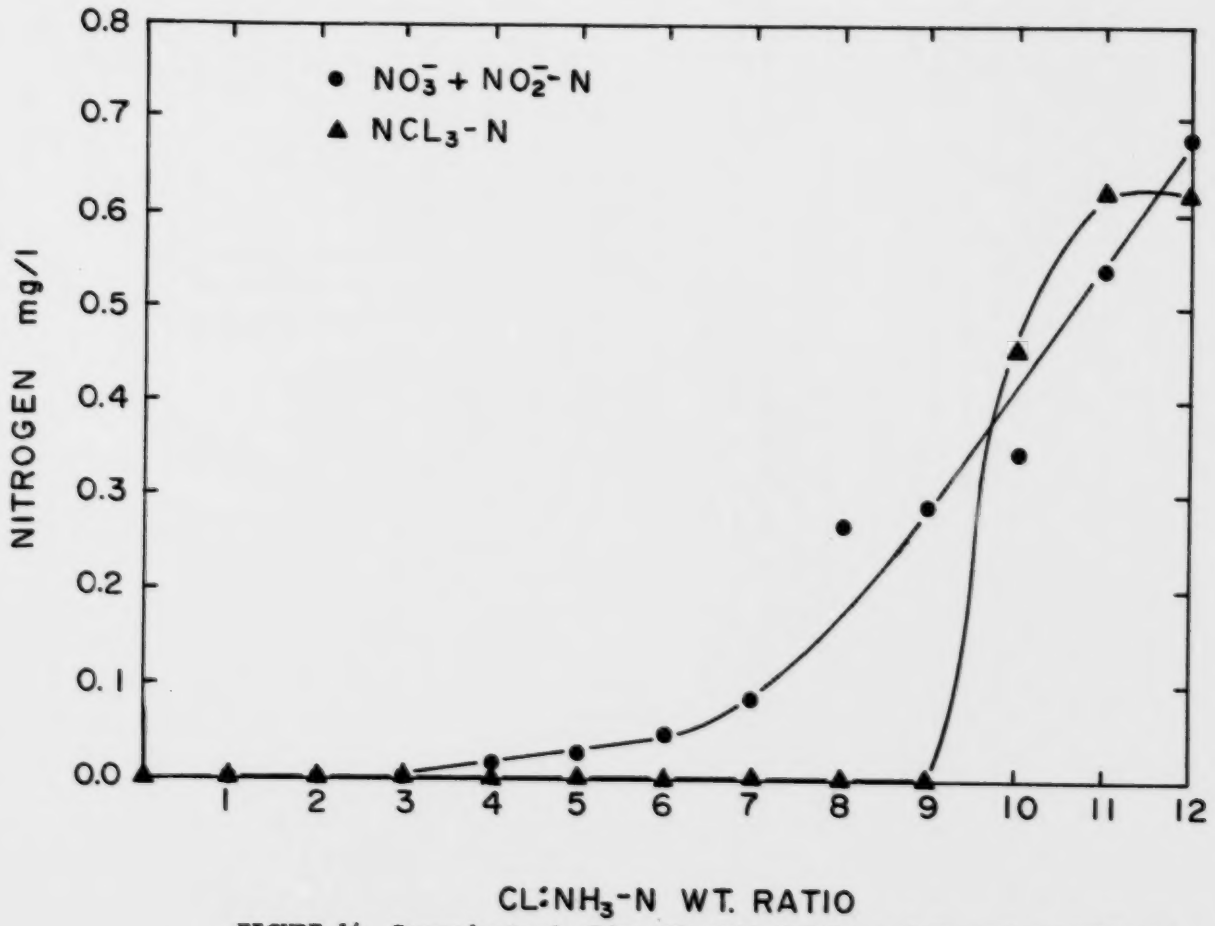


FIGURE 14 Byproducts in Lime Clarified Filtered Secondary Effluent

SECTION VIII

PILOT PLANT CHLORINATION

During construction of the breakpoint chlorination system, chlorination was attempted in the pilot plant using an eductor to mix chlorine water and wastewater in a 2 inch diameter pipe. The NH_3-N ranged from 3.0 to 9.4 mg/l and the flow rate was 20 gal./min. Base was premixed in the water upstream of the eductor to maintain the effluent in the 7-8 pH range. Samples were taken 6 ft. downstream of the eductor. Breakpoint was not achieved and excessive NCl_3 formation occurred. A comparative test in the laboratory with good mixing achieved breakpoint. Thus, the eductor did not provide adequate mixing.

Initial runs on the breakpoint chlorination system (Figure 1) in the Pilot Plant were made with filtered secondary effluent. Breakpoint occurred at a $Cl:NH_3$-N weight ratio between 8:1 and 9:1. In repeated tests (Table 2) the influent NH_3-N concentrations ranging from 12.9 to 21.0 mg/l, were reduced to less than 0.1 mg/l.

Typical caustic requirements for filtered secondary effluent in the pH range 6.0 to 7.9 (Table 3) at approximately a 9:1 $Cl:NH_3$-N dosage ratio increased with increasing reaction pH from 0.88 pounds of NaOH per pound of Cl_2 at pH 6.0 to 1.67 pounds per pound at pH 7.9. At pH 7, 1.3 pounds of NaOH were used per pound of Cl_2. Calcium hydroxide solution was also used and the quantities of calcium hydroxide needed were found to be in stoichiometric proportion to the NaOH requirement. Since the breakpoint stiochiometry to neutralize the acid produced at pH 7 requires 1.5 pounds of NaOH per pound of Cl_2, the neutralization at pH 7 with 1.3 pounds of NaOH per pound of Cl_2 must have used some of the wastewater alkalinity.

The secondary wastewater was analyzed to determine the amounts of undesirable products. The amount of nitrate produced (Table 4) did not exceed 1.2 mg/l. The formation of nitrate was minimized by operating in the lower pH range near pH 6. The amount of nitrogen trichloride formed did not exceed 0.43 mg/l. As in laboratory tests, however, the formation of nitrogen trichloride increased with decreasing pH. More importantly, the NCl_3 concentration increased sharply with increasing chlorine dosage above the breakpoint (Table 5). Because NCl_3 formation was more dependent on chlorine dosage than on pH, operation at above pH 7, with good mixing and good chlorine dosage control, however, produced only small amounts of NCl_3 and NO_3^-. (If good chlorine dosage control is not achieved, operation at pH 8 can be employed to minimize the noxious NCl_3 formation but will result in slightly or higher NO_3^--N residuals and increased usage of base).

Chloride ion, a direct product of the reaction, was added to the product water as NaCl or $CaCl_2$. The Stiochiometry revealed that with

Table 2. Breakpoint Chlorination of filtered Secondary Effluent

NH_3-N mg/l				
Influent	Effluent	pH	$Cl:NH_3$-N Wt. Ratio	Free Cl mg/l
13.9	0.1	6.0	8.4:1	7.0
20.3	0.1	6.0	8.8:1	6.5
21.0	0.1	7.0	8.5:1	2.0
12.9	0.1	7.0	9.0:1	3.4
17.0	0.1	7.5	9.2:1	8.5
15.4	0.1	8.0	8.4:1	2.5

Table 3. Caustic Requirements for Breakpoint Chlorination of Filtered Secondary Effluent

pH	$\frac{\text{pounds NaOH}}{\text{pound } Cl_2}$	$Cl:NH_3$-N wt. ratio
6.0	0.88	8.8:1
7.0	1.3	9.0:1
7.9	1.67	9.0:1

Table 4. Nitrate Formation in Filtered Secondary Effluent

pH	NH_3-N in mg/l	NO_3^--N mg/l	% NO_3^--N of influent NH_3-N
6.0	13.9	0.5	3.6%
6.0	20.3	0.8	3.9%
7.0	17.0	0.9	5.3%
7.0	16.1	0.8	5.0%
7.9	20.3	1.2	5.9%
8.0	15.4	0.9	5.9%

Table 5. Nitrogen Trichloride Formation in Filtered Secondary Effluent

pH	NH_3-N in mg/l	Cl:NH_3-N wt. ratio	NCl_3-N mg/l
6.0	20.3	8.75:1	0.33
7.0	17.0	10.0:1	0.05
7.0	16.1	12.0:1	0.43
7.5	17.0	9.2:1	0.05
7.9	20.3	9.0:1	0.05

an influent NH_3-N concentration of 15 mg/l and at Cl:NH_3-N ratio of 9:1, approximately 220 mg/l of NaCl was produced.

The lime clarified and filtered raw wastewater was continuously breakpointed over a 5 month period in the pilot system. The feed from filtration to the chlorination process had a pH of 9-10.

During the study, TKN and NH_3-N removals (Table 6) generally revealed that breakpoint chlorination removed chiefly NH_3-N with the organic nitrogen little affected by chlorine. The dissolved organics were likewise unaffected by chlorination as the TOC did not change appreciably through the system.

In the first month of operation with an influent pH of 9 to 10 and without pH preadjustment, the average NH_3-N concentrations in the influent and effluent were 12.5 mg/l and 1.2 mg/l, respectively (Table 6). The NaOH usage was 0.9 pounds per pound of chlorine. NO_3^- in the effluent was 0.8 mg/l.

Control of pH was difficult with an influent pH of approximately 10. Instead of maintaining a steady value of 7.0, the pH periodically cycled between 6.0 and 8.0 with occasional high pH above 8. The daily NH_3 variations in the effluent (Figure 15) revealed that a NH_3 breakthrough occurred periodically. The NH_3-N breakthrough coincided with periods of high pH.

The operating difficulties occurred because of instability in the process pH control loop. The instability was caused by the large detention time of about 8 minutes in the reactor with poor mixing in the upper part of the tank. The instability on pH control could be minimized by reducing with either CO_2 or Cl_2 the pH of the influent feed to approximately that desired in the breakpoint before entering the breakpoint reactor.

In the next three months with CO_2 preadjustment of the pH to 7, the controller consistently maintained the pH at 7.0 for a steady flow rate of 25 gpm. With effective pH control, the daily NH_3-N variation in the effluent (Figure 15) revealed consistently good NH_3-N removal. The average influent and effluent concentrations for this period were 11.0 mg/l and 0.3 mg/l of NH_3-N. The NO_3^- in the effluent averaged 0.6 mg/l.

The NH_3-N removals represented a significant improvement over the first month's operation. However, the NaOH usage increased to 1.8 pounds per pound of chlorine (Table 6). The increased base requirement occurred because the CO_2 converted the OH^- alkalinity at pH 10 to HCO_3^- alkalinity at pH 7. With the system controlled at pH 7, the bicarbonate alkalinity was not available for neutralizing the acid produced in the breakpoint reactions. The stiochimetric base requirement is 1.5 pounds of NaOH per pound of Cl_2. Thus excess CO_2 also appeared to exert an additional base demand.

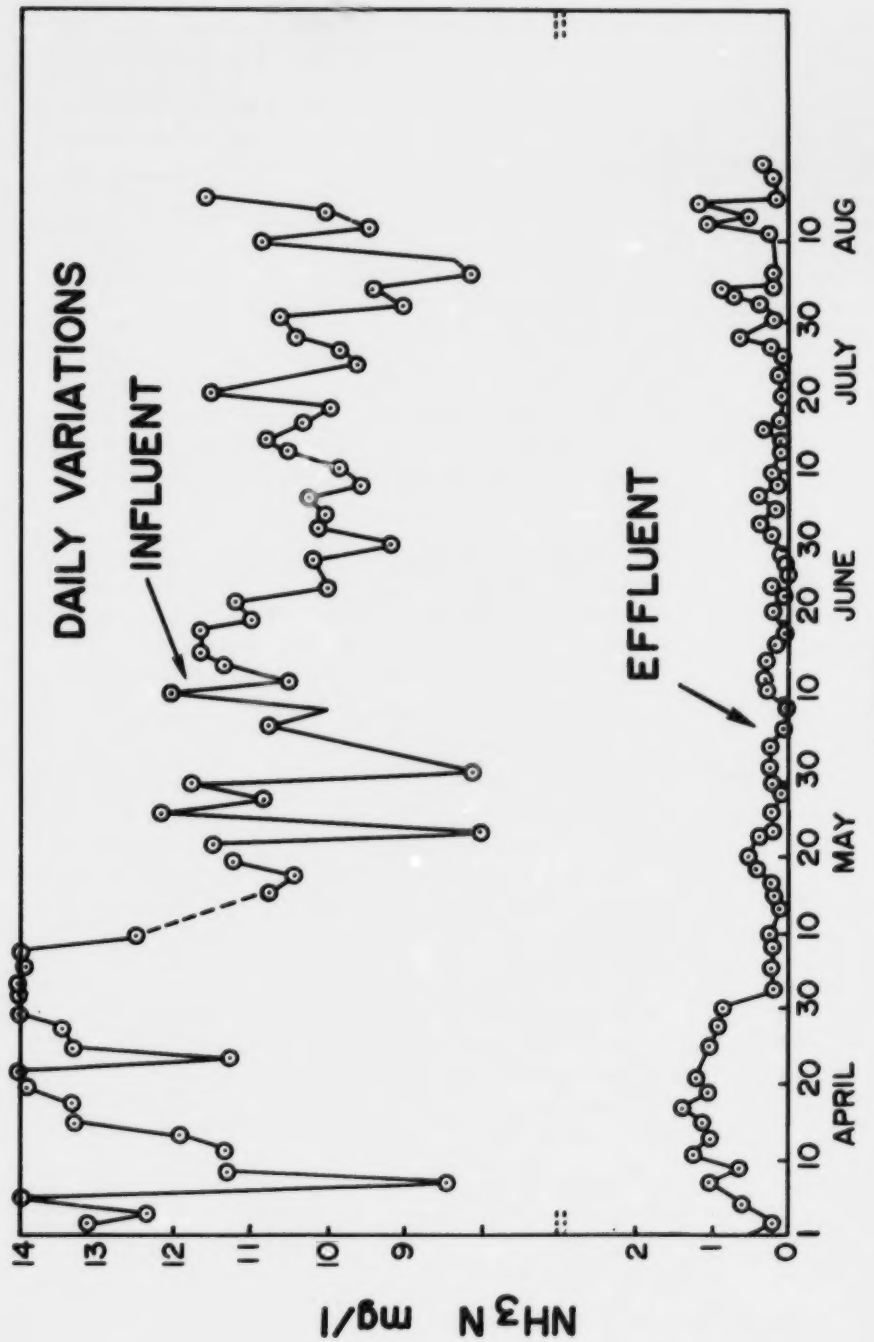


FIGURE 15 Daily NH_3-N Removal Variations

TABLE 6

Continuous Breakpoint
of
Lime Clarified and Filtered Raw Wastewater

Month	April	May	June	July	August
Flow, gpm	25	25	25	25	22.5-55.5
Influent					
pH	9.9	9.3	9.3	9.2	9.0
P. alk, mg/l	70	45	54	31	30
M.O., alk., mg/l	140	84	96	82	80
NH_3-N mg/l	12.5	11.6	10.8	10.4	9.7
TKN-N, mg/l	14.2	14.1	12.2	11.9	10.7
NO_3^--N, mg/l	0.16	0.02	0.0	0.0	0.0
TOC, mg/l	22.6	19.9	16.7	17.0	18.3
pH Adjustment	None	CO_2	CO_2	CO_2	Cl_2
pH after Adj.	9.9	7.0	7.0	7.0	7.0
Reaction Conditions					
pH	7.0	7.1	7.2	7.3	--[1]
Cl:N, lb/lb.	9:1	9:1	9:1	9:1	9:1
NaOH:Cl, lb/lb.	0.9	1.8	1.8	1.8	--[1]
Effluent					
M.O., alk., mg/l	52	100	124	118	60
NH_3-N mg/l	1.2	0.4	0.4	0.4	0.5
TKN, mg/l	4.8	2.5	2.0	1.8	2.1[1]
NO_3^--N, mg/l	0.8	0.7	0.6	0.5	0.5
TOC, mg/l	23.1	20.1	18.8	18.8	16.9

[1] pH cycled with poor process control; breakpoint was frequently lost. Data represents periods of successful breakpoint; base requirement and pH not accurately determined.

In further evaluation of these results, a brief review of the neutralization reactions is needed. The breakpoint chlorination reactions produce acid which must be neutralized to maintain a neutral reaction medium and to prevent the formation of undesirable side products. To reduce process cost, the use of the alkalinity present in the wastewater to neutralize part of the acid produced is needed.

The types of alkalinity present in the wastewater include OH^- alkalinity at high pH and HCO_3^- alkalinity at neutral pH. The hydroxide alkalinity, a strong base, neutralizes the acid directly without buffer effects.

$$OH^- + H^+ \longrightarrow H_2O \qquad (8)$$

The HCO_3^- alkalinity, a weak base, neutralizes the acid by forming CO_2 (equation 9). At the reaction pH of 7.0, CO_2 is reconverted by the base added for pH control to HCO_3^- ions. Thus, little HCO_3^- alkalinity is available for neutralization in a single stage breakpoint reactor controlled at pH 7.

$$OH^- + CO_2 \longrightarrow HCO_3^- \qquad (9)$$

The alkalinity values in the influent and effluent (Table 6) indicated whether the alkalinity present in the wastewater was utilized for acid neutralization. In the first month of operation at pH 10, with the stoichiometric requirement of 1.5 pounds of NaOH per pound of chlorine, only 0.9 pounds of NaOH were used per pound of chlorine. Thus, the OH^- alkalinity present in the wastewater at pH 9-10 satisfied part of the base demand and was indicated by a decrease in alkalinity across the system (Table 6). In the next three months of operation, CO_2 needed in pH preadjustment for effective control converted the OH^- alkalinity into HCO_3^- alkalinity (equation 9) which was unavailable for acid neutralization in the breakpoint chlorination system operated at pH 7.0. Hence, NaOH usage increased to 1.8 pounds per pound of chlorine. In this case, the base requirement was 0.3 pounds more than the stoichiometric value of 1.5 pounds because of the additional base demand exerted by excess CO_2. The increase in alkalinities across the system (Table 6) confirmed the conversion of excess CO_2 to bicarbonate ion.

The HCO_3^- alkalinity present in the wastewater, however, may be used for neutralizing acid (equation 10).

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \qquad (10)$$

If chlorine is used in a two-step breakpoint system at a dosage not to exceed that for the formation of monchloramine (5:1 Cl_2:NH_3-N) in the first stage, and acid formed during the reaction produces CO_2 at a lower pH such as 6. The CO_2 is then stripped from the water before additional chlorine and base is added in a second reactor operated at

pH 7.0. This two stage approach has its greatest potential in a wastewater with appreciable HCO_3^- alkalinity such as secondary effluent with a pH near 7 but may also be applied to the lime clarified raw wastewater.

During the last stage of operation with chlorine to preadjust the pH a diurnal flow variation was also applied to the system. With the system on a diurnal flow, pH control was very difficult. The daily average NH_3-N variation in the effluent (Figure 15) revealed the highest NH_3-N breakthrough during the entire 5 months of operation. The monthly average NH_3-N concentrations in the influent and effluent were 10.2 mg/l and 2.1 mg/l. While the use of Cl_2 in pH preadjustment probably reduced base requirements, the base usage during this stage of operation could not accurately be determined because of frequent loss of breakpoint as the pH cycled. Thus, an improved control system was needed to operate the split chlorine treatment approach and to handle the diurnal cycle. The chlorine reactor with large detention time and inefficient mixing caused the pH to cycle.

To provide improved process control and a flexible system for use on both lime treated (pH 10) and secondary wastewaters (pH 7), a two stage chlorination system is proposed to replace the existing pilot system. The proposed system may be used as either single or two stage operation on the limed wastewaters (pH 10 and above). The two stage system includes influent pH adjustment in a 1.6 second (average) static mixer by prechlorination followed by CO_2 stripping in the existing reactor tank and a 1.6 sec static mixer as the breakpoint reactor. The complete system also includes the complex process control system as described in the subsequent section. The proposed system with process control instrumentation needs to be installed and evaluated.

SECTION IX

INSTRUMENTATION AND PROCESS CONTROL

The amount of chlorine required for breakpoint depends upon the ammonia, and non-ammonia chlorine demand, and the amount of residual free chlorine desired in the wastewater.

The control of breakpoint chlorination in wastewater is more complex than most industrial control systems because of the inherent variability of the wastewater and the wastewater flow. The inlet ammonia concentration, wastewater flow, and wastewater alkalinity, will vary sharply with time. The chlorine dosage must be set and controlled in proportion to the ammonia feed. With too low a chlorine dosage, the reaction will not go to completion and chloramines will be the end product. Nitrogen trichloride will be formed if more than a little excess chlorine (beyond that needed for breakpoint) is added to the system, especially if the pH is allowed to drop to below 6, or if complete and rapid mixing is not achieved.

The instrumentation system employed in the study is shown in Figure 16. The flow to the system is measured by the magnetic flow meter. The NH_3-N concentration in the influent is measured by the Technicon Auto Analyser #1. The Cl_2 dose to the reactor is set manually at approximately a 9:1 $Cl:NH_3$-N weight ratio. The free residual chlorine in the effluent is measured by the Technicon Auto Analyser #2. This reading is used to manually trim the initially set (9:1 weight ratio) Cl_2 dose so as to constantly maintain a small smount (2-4 mg/l) of free residual chlorine in the effluent.

There are two control loops in the system. The first loop is for the pH reduction from 10.0 to 7.0. The response time is of the order of one-half second and the pH control is very good. The second pH control loop is the 1 to 2% NaOH solution feed to maintain a pH of 7.0 in the reactor. The response time in the second pH loop is of the order of 8 minutes and a steady pH is maintained with difficulty.

Thus, the EPA-DC Pilot Plant staff proposed a controller design to completely automate and to improve control of breakpoint chlorination. The proposed control system establishes an approximate chlorine dosage for breakpoint chlorination of ammonia and modifies the approximate chlorine dosage to the optimum chlorine dosage required for complete removal of ammonia by breakpoint chlorination from a specific wastewater. The function of the breakpoint computer controller is described by the following equation:

$$(A \cdot B \cdot C)(f\ [D\text{-}E]) = F$$

A = Process flow in liters per minute

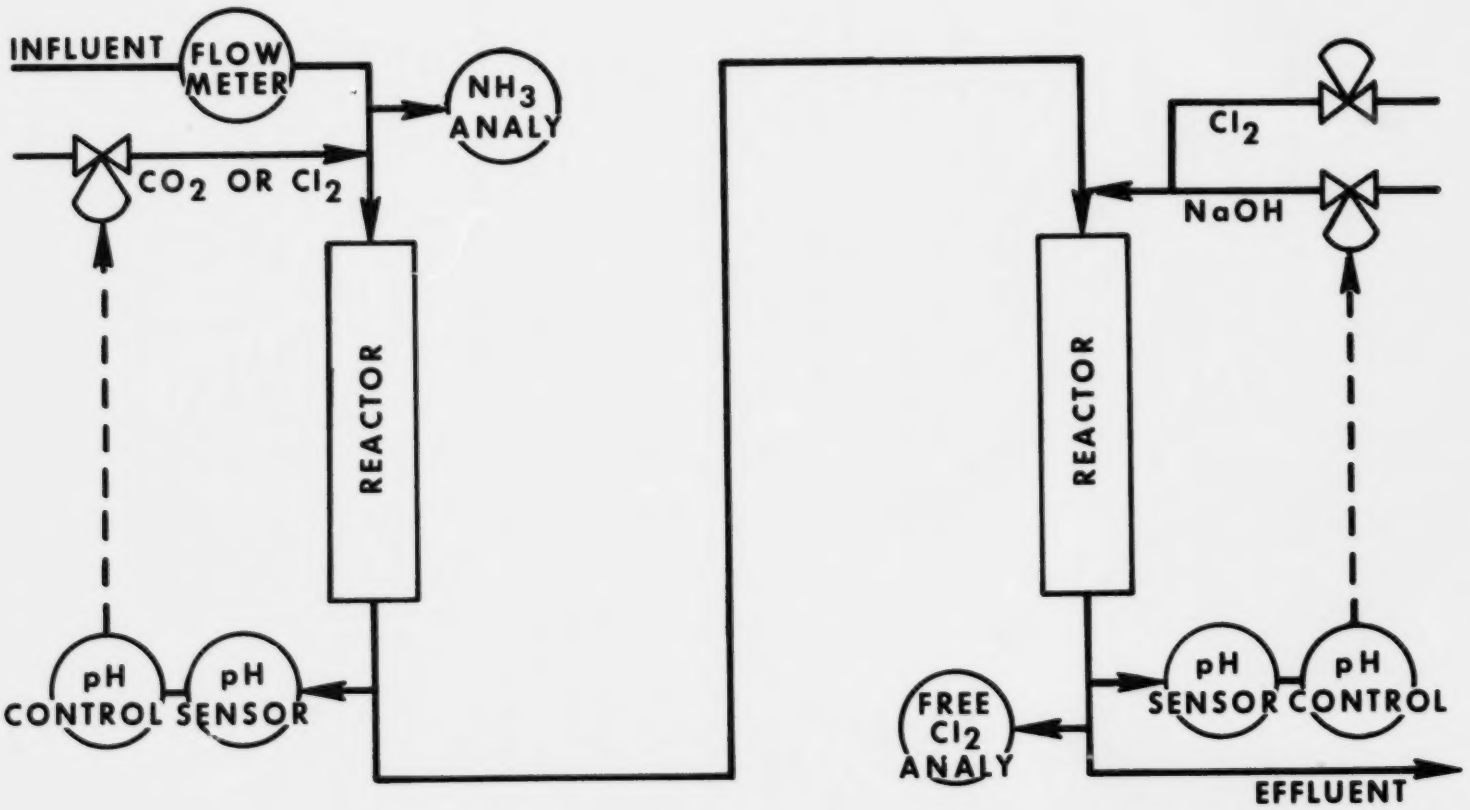


FIGURE 16 BREAKPOINT CHLORINATION INSTRUMENTATION

B = NH_3-N concentration, mg/l

C = Preselected Cl:NH_3-N weight ratio

D = Set point free chlorine residual, mg/l

E = Measured free chlorine residual, mg/l

F = Total chlorine dosage, grams/min.

$f[D-E]$ = Controller signal based upon deviation of measured free chlorine residual from setpoint

As shown in Figure 16, process flow (A) is measured by a flow meter. A continuous measurement of the ammonia concentration (B) in the influent stream is made by an automatic analyzer. This automatic analyzer may operate colorimetrically or use a specific electrode. The two linear signals (A & B, flow and ammonia concentration) are multiplied by a manually preselected value (C) by the breakpoint controller to establish an approximate chlorine requirement ($A \cdot B \cdot C$) to achieve breakpoint chlorination. The manually preselected value (C) corresponds to the Cl:NH_3-N weight ratio required for the ammonia oxidation to N_2 and has a theoretical value of 7.6:1. The selected value depends upon the wastewater, and usually varies from 8-10:1.

The free chlorine concentration in the process effluent (E) is automatically measured and the free chlorine signal thus determined is compared to a setpoint free Cl_2 residual (D) by a standard process controller. The difference signal (D-E) is used by the breakpoint computer-controller in a feedback loop to modify the chlorine requirement established by the mass signal ($A \cdot B \cdot C$) to the optimum chlorine dosage (F) required for complete ammonia removal and for the desired free chlorine residual.

Careful pH control is necessary to prevent the formation of noxious by-products and to stabilize the process pH for efficient breakpoint operation. Control of pH is achieved by the proper addition of a base to neutralize the acid formed by addition of chlorine to the process. The pH of the system depends upon both the alkalinity of water, the flow, and the total chlorine dose. Simple feedback pH control does not prevent cycling in the wastewater pH because of the wide variations in flow and operating conditions. In the proposed system, the pH may be maintained by a combined feed forward and feedback control system as described by the following equation:

$F \cdot G = H$

F = Signal proportional total chlorine dosage

G = Output pH error signal (difference from manually selected pH setpoint)

H = Signal proportional to change in base dosage

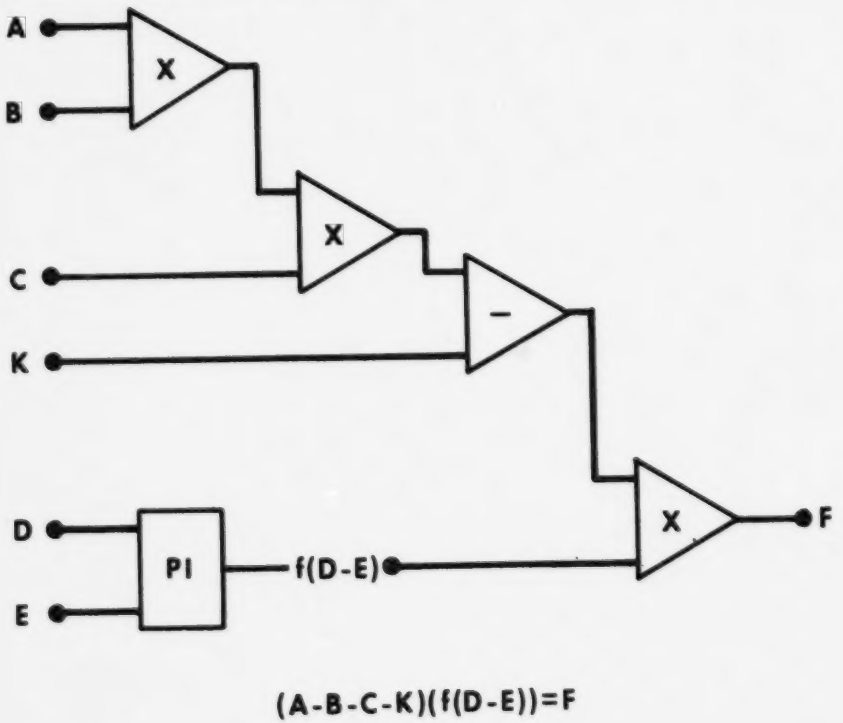
The pH of the process effluent is measured and transmitted to the pH controller with an automatic pH analyzer. The pH controller produces a pH error signal proportional to the difference between the measured pH and the selected pH control point (setpoint). The pH error signal is multiplied by the signal from the chlorine breakpoint controller that is proportional to the total chlorine dose. The product signal is proportional to the amount of base required for pH control and controls the base feed to the reactor. The control system thus minimizes upsets in process pH caused by changes in chlorine dose, flow and alkalinity of the wastewater.

As may be seen in Figure 17, the breakpoint computer-controller is basically a series of multiplying and dividing function generators and a process controller. These operations can be performed pneumatically or electronically by analog or digital equipment. The breakpoint computer-controller receives signal A from the flow meter, signal B from the ammonia analyzer and multiplies the product of A and B times a manually selected factor C corresponding to the $Cl:NH_3$-N weight ratio required for the ammonia oxidation to N_2. The resulting signal from the product of A, B and C is used to control the chlorine feed to the process until a free chlorine residual is sensed. When a free residual chlorine signal is sensed and compared to free chlorine setpoint in a process controller, the controller feedback signal f[D-E] is combined with that of the feed forward chlorine demand (A·B·C) to control the chlorine dosage and maintain the desired free chlorine residual. As long as a free chlorine residual is not sensed (i.e., initial start-up), the $Cl:NH_3$-N weight ratio (C) must be manually increased until a free chlorine residual is obtained.

After a free chlorine residual has been obtained and the appropriate $Cl:NH_3$-N weight ratio selected (for the specific wastewater), the fluctuations in the flow or influent ammonia concentrations will automatically cause a corresponding change in chlorine dosage computed by the A·B·C signal. Fluctuations in the process chlorine demand other than flow or ammonia fluctuations (i.e., organic chlorine demand) will cause a corresponding change in the [D-E] signal and thus maintain the selected free chlorine residual.

In an alternate embodiment of the control system, the alkalinity of the influent wastewater is utilized to neutralize the acid formed by the addition of chlorine, reducing both base requirements for pH control and effluent wastewater alkalinity. The effect is achieved by predosing with chlorine to a manually selected pH level.

The breakpoint computer-controller establishes a theoretical chlorine dosage for breakpoint chlorination of ammonia, as described in the previous system, subtracts the chlorine predose required for pH adjustment (if any) and modifies the approximate chlorine dosage to the



A=PROCESS FLOW RATE,1/min.

B=NH_3-N CONCENTRATION, mg/l

C=PRESELECTED Cl:NH_3-N WEIGHT RATIO

D=PREDETERMINED FREE CHLORINE RESIDUAL,mg/l

E=MEASURED FREE CHLORINE RESIDUAL,mg/l

F=TOTAL CHLORINE DOSAGE, grams/min.

K=CHLORINE PREDOSE, grams/min.

f(D-E)=ANALOG P.I. CONTROLLER OUT PUT

▷ =PNEUMATIC OR ELECTRONIC FUNCTION GENERATOR

$$(A-B-C-K)(f(D-E))=F$$

FIGURE 17 BREAKPOINT COMPUTER CONTROLLER

optimum dosage required for complete removal of ammonia by breakpoint chlorination of a specific wastewater. The function of this alkalinity-breakpoint computer-controller is described by the following equation:

$$(A \cdot B \cdot C - K)(f\ [D-E]) = F$$

A = Process flow rate, l/min.

B = NH_3-N concentration, mg/l

C = Preselected Cl:NH_3-N weight ratio

D = Predetermined free chlorine residual, mg/l

E = Measured free chlorine residual, mg/l

F = Total chlorine dosage, grams/min.

K = Chlorine predose, grams/min.

f[D-E] = Controller signal based upon deviation of measured free chlorine residual from setpoint.

Prechlorination dosage (K) is a function of the pH and buffer capacity of the particular wastewater influent. An approximate predose is either calculated for a specific wastewater or determined empirically. This approximate amount is refined by an error signal from a flow proportioned pH controller at the effluent side of the predose reactor. The chlorine predose (K) is continuously measured and subtracted from the product of the A·B·C signal by the breakpoint computer-controller. The resulting (A·B·C-K) signal is then modified by the [D-E] signal as described in the first embodiment.

With reference to the control system described, the quantities A, B, C K and f [D-E] are available in the form of electronic signals. The evaluation of the proposed control systems in the pilot plant only requires that the computer-controller be constructed and installed to operate on the signal from existing sensors.

SECTION X

COSTS

Itemized costs are given in Table 7. The calculations are based on a 300 MGD plant assuming an average ammonia-nitrogen concentration in the influent of 15 mg/l. Chlorine and lime costs are $75 and $24 per ton, respectively. Annual capital costs are computed at an annual rate of 8% including interest and amortization.

Table 7. Breakpoint Chlorination Costs

	Cents/1000 gal.
Electricity (Mechanical Mixing)	.50
Chemicals	
Chlorine (135 mg/l)	4.22
Lime (1 lb/lb Cl_2)	1.35
Supplies	.05
O & M Labor	.60
Capital Charges	.60
Total	7.32

SECTION XI

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SECTION XII

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